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**An analytical model for chemical diffusion in layered
contaminated sediment systems with bioreactive caps**

Huaxiang Yan¹, Jiawei Wu¹, Haijian Xie^{1*}, Hywel R. Thomas², Shijin Feng³

¹Institute of Hydrology and Water Resources Engineering, Zhejiang University, 866 Yuhangtang
Road, Hangzhou, 310058, China

²Geoenvironmental Research Centre, School of Engineering, Cardiff University, The
Queen's Buildings, Newport Road, Cardiff, CF243AA, UK, professor, FRS,
FREng, ThomasHR@cardiff.ac.uk

³Department of Geotechnical Engineering, Tongji University, Shanghai, 200092,
China, professor, fsjgly@tongji.edu.cn

*Corresponding author: xiehaijian@zju.edu.cn; Tel.: +86-571-88981608; Fax: +86-571 88208793

Abstract

An analytical model for contaminant transport in multi-layered capped contaminated sediments including the degradation of organic contaminant is presented. The effect of benthic boundary layer was treated as a Robin-type boundary condition. The results of the proposed analytical model agree well with experimental data. The biodegradation of contaminant in bioturbation layer shows a significant influence on the flux at the surface of system. The maximum flux for the case with $t_{1/2,bio}=0.07$ year can be 4.5 times less than that of the case without considering the effect of biodegradation. The thickness of bioturbation layer has a significant effect on the performance of the capped contaminated sediment. The maximum flux for the case with $l_{bio}=15\text{cm}$ can be 17 times larger than that of the case without bioturbation layer. This may be due to the fact that the effective diffusion coefficient of sand cap can be 28 times lower than D_{bio} . The mass transfer coefficient should be considered for the design of the capping system as the contaminant concentration at the top of system for the case with $k_{bl}=2.5\times 10^{-5}\text{ cm/s}$ can be 13 times greater than that of the case with $k_{bl}=10^{-4}\text{ cm/s}$. The proposed analytical model can be used for verification of complicated numerical methods, evaluation of experimental data and design of the capping contaminated sediment systems with reactive cap layers.

Keywords: Analytical model; chemical diffusion; degradation; capped contaminated sediment; mass transfer coefficient; bioturbation layer

1. Introduction

Sediments contaminated with organic compounds are always found in many waterways, harbors and estuaries^{1,2}. The transfer of these chemicals from the sediments into overlying waters will affect the marine food web and the human using these waters for recreation and supply of sea food. In order to reduce risk associated with contaminant in the sediments, different remediation strategies have been developed. The general characteristics of the three basic sediment management options are natural recovery, capping or in situ treatment, and dredging². In order to isolate the contaminants from organisms in the water and surficial sediments, in-situ capping is used as a cover for placement over contaminated sediment³. The cap can be constructed with multiple layered clean sediments such as sand and gravel^{1,2,4,5}. The application of sand and sediment caps as a remediation technology for contaminated sediments was subsequently investigated. Wang et al.⁴ and Thoma et al.⁶ found that a layer of clean sand sediment successfully reduced the concentrations of the HOC 2,4,6-trichlorophenol in the laboratory.

The traditional sand caps are less effective at sites where groundwater seepage or mobile contaminants are present⁷. The active caps incorporating reactive or sorptive constituents are designed to reduce contaminant flux⁸⁻¹⁰. For instance, the coke and other “active” materials (e.g., activated carbon and kraft lignin) are used as capping to enhance sorption in order to reduce the availability of the contaminant and improve the effectiveness of in situ capping^{5,11-15}. The isolation times provided by the sorbent layers increased with the increase of sorption strength and capacity (activated

58 carbon>> coke \approx soil>> sand)⁵. Eek et al.¹ developed the laboratory microcosm test to
59 measure the diffusion of PAHs and PCBs from sediment with different capping layers.
60 They found that caps with passive material can significantly reduce the diffusive
61 contaminant flux through the cap.

62 It has been shown that diffusive transport is often the dominant mode of
63 contaminant transport through subaqueous caps for contaminated sediments since the
64 water flow in fine-grained sediments is very slow^{4, 16, 17}. Diffusion of contaminant
65 through layered porous media is often modeled by numerical methods. For instance,
66 Rowe et al.¹⁸ have developed the finite layer methods for contaminants transport
67 through multi-layered barrier systems. Leo and Booker¹⁹ developed the boundary
68 element method for contaminant diffusion in non-homogeneous porous media.
69 Praveen Kumar and Dodagoudar²⁰ provide an accurate methodology for numerical
70 simulation of the two-dimensional contaminant transport through the saturated
71 homogeneous porous media and landfill liners using element-free Galerkin method
72 (EFGM). The finite element method based numerical model COMPASS has also been
73 used for the analysis of contaminant diffusion in the layered porous media²¹⁻²⁴. Zhang
74 et al.²⁵ investigated contaminant transport in the two-layered system consisting of
75 compacted clay liner and the aquifer using the numerical method including the
76 finite-difference method and the numerical inversion of Laplace transform. However,
77 the use of the numerical models is restricted to experienced users and for sites where
78 field data are known in great detail.

79 Analytical solutions play an important role in understanding many scientific
80 phenomena²⁶⁻²⁸, although some simplifications need to be made in the process of
81 deriving them. In particular, analytical solutions can also play a unique role in
82 validating many new numerical methods²⁹⁻³¹. For these reasons, analytical solutions
83 have been derived in recent years for many scientific and engineering problems³²⁻³⁴.
84 This means that by using analytical solutions in this particular study, a better
85 understanding of the mechanism of contaminant diffusion can be explored, the
86 movement of contaminant plumes can be predicted, and the results of numerical
87 modeling can be verified³⁵. They are also more computationally efficient and can be
88 used to address the Robin-type boundary condition that is often not available in the
89 numerical programs^{37,38}. Some works have been done on solving the diffusion or
90 advection-dispersion equation of solute transport in two- or multi-layered porous
91 media using the Laplace transform method³⁸, the integral transform method³⁹, and an
92 approach combining the Laplace transformation method and binomial theorem⁴⁰. An
93 analytical solution for contaminant diffusion through multi-layered system was
94 presented by Chen et al.⁴¹. Li and Cleall³⁷ presented analytical solutions for various
95 combinations of fixed solute concentration and zero-flux boundary conditions applied
96 at each end of a finite one-dimensional domain considering arbitrary initial solute
97 concentration distribution throughout the media. Deng et al.⁴² proposed the integral
98 transform solution for solute transport in multi-layered porous media with the implicit
99 treatment of the interface conditions and arbitrary boundary conditions. Zhao and his
100 coworkers have conducted extensive studies to derive analytical solutions for both

chemical dissolution front instability problems⁴³⁻⁴⁸ and physical dissolution front instability problems⁴⁹ in fluid-saturated porous media. However, the effect of degradation on the transport of contaminant was not considered in the literature analytical models.

Many types of organic contaminant (e.g., aliphatic and aromatic compounds) can be significantly degraded in soils⁵⁰⁻⁵³. For the sediment capping systems, Lampert and Reible⁵⁴ reported that degradation of sediment contaminant in the biologically active capping may be of primary importance for the control of the contaminant release from the sediments. Himmelheber et al.¹⁰ demonstrated that in situ bioreactive capping can be a feasible remedial approach for the contaminated sediments. Thoma et al.⁶ also found that degradation of contaminant in sediment has a great influence on contaminant flux discharged. For example, the maximum flux released for the case with half-life of 100 years in the sediment can be 67 times lower than the case without considering degradation. Therefore, it is of great importance to consider the degradation process to impede contaminant release from the sediment. In addition, the boundary condition at the cap-water interface is quite complex, as it essentially requires the effluent boundary condition from a porous medium; therefore, the surface boundary condition for the capping sediment systems is often modeled with a mass transfer coefficient². Thibodeaux⁵⁵ and Boudreau and Jørgensen⁵⁶ presented empirical correlations for mass transfer coefficient based on mixing conditions in the overlying water. The value of mass transfer coefficient should be conservatively estimated, as its value directly affects the surficial sediment concentrations⁵⁴. However, few

analytical models have considered the effect of mass transfer coefficient on contaminant transport through the contaminated sediment and the capping layer.

The objective of this paper is to develop an analytical model for contaminant transport in multi-layered capped sediment system considering the effect of contaminant degradation, diffusion, and adsorption. The effects of bioturbation layer on contaminant transport in capped contaminated sediment system will be analyzed by using the mass transfer coefficient at the cap-water interface. The analytical solutions are compared with an observed contaminant flux. Based on the analytical solutions, the effect of degradation of organic contaminant and mass transfer coefficient on contaminant transport in capped contaminated sediment system will be analyzed.

2. Mathematical model

The analytical model for contaminant diffusion in the multi-layered capped contaminated sediment system was developed based on the following assumptions:

1. Contaminant diffusion is one-dimensional and follows Fick's second law.
2. The porous medium is isotropic, homogeneous and saturated.
3. Adsorption is a linear and equilibrium process.
4. Biodegradation model of organic contaminant in the medium is based on first-order kinetics. Due to its mathematical simplicity, its easy implementation into transport models, and the necessity of determining only a single parameter, the biodegradation model most frequently used is first-order kinetics⁵⁷.

Based on the above assumptions, one dimensional model for organic contaminant in a finite composite media of M layers is developed (see Fig. 1). The thickness of m layer is l_m . The system consists of the contaminated sediment, the capping layers and the benthic boundary layer. The governing equations of contaminant transport in the soils can be expressed as¹⁸:

$$R_{dm} \frac{\partial C_m}{\partial t} = D_m^* \frac{\partial^2 C_m}{\partial z^2} - \lambda_m C_m \quad (m=1, 2, 3, \dots, M) \quad (1)$$

where $C_m(z, t)$ is the concentration of contaminant in soil layer m ; D_m^* is the effective diffusion coefficient in the soil layer m ; R_{dm} is retardation factor of the soil layer m ; z is the coordinate with downward positive; t is time; and λ_m is the biodegradation rate¹⁸:

$$\lambda_m = \ln 2 / t_{1/2} \quad (m=1, 2, 3, \dots, M) \quad (2)$$

where $t_{1/2}$ is the half-life of contaminant in the soil layer m .

At the interface between soil layer m and $m+1$, the concentration and flux of the contaminants are continuous^{37, 41, 58, 59}:

$$C_m(L_m, t) = C_{m+1}(L_{m+1}, t) \quad (m=1, 2, 3, \dots, M-1) \quad (3)$$

$$n_m D_m^* \frac{\partial C_m(L_m, t)}{\partial z} = n_{m+1} D_{m+1}^* \frac{\partial C_{m+1}(L_{m+1}, t)}{\partial z} \quad (m=1, 2, 3, \dots, M-1) \quad (4)$$

where n_m is the porosity of soil layer m ; L_m is the distance of layer m , $L_m = l_1 + l_2 + \dots + l_m$.

For the top surface boundary, a Robin-type boundary condition is applied. The bottom condition is a type of Neumann boundary condition. The boundary conditions for the problem can then be expressed as follows^{6,60}:

$$\frac{\partial C_1(0, t)}{\partial z} = 0 \quad (5)$$

$$D_M^* \frac{\partial C_M(L_M, t)}{\partial z} = k_{bl} C_M(L_M, t) \quad (6)$$

where k_{bl} is the mass transfer coefficient in the benthic boundary layer. Eq.5 is mathematically known as a second-type or Neumann boundary condition and represents an impermeable base stratum. This bottom boundary may be assumed to not allow any transmission of contaminant⁵⁸. Eq.6 is known as the Robin-type boundary condition which is taken as a flux-matching relationship between the top of the sediment cap and the benthic boundary layer⁵⁴. When k_{bl} tends to be infinite, the top boundary condition tends to be a zero concentration boundary condition. However, when k_{bl} tends to be 0, the top boundary condition would tend to be a zero flux boundary condition. This indicated that the mass transfer coefficient has a great influence on contaminant transport in the capped sediment system. It is also indicated that the analytical solution of this paper can be applied to the situation of zero concentration boundary condition and zero flux boundary condition (i.e., Eq. 5).

The following equation can be used to estimate k_{bl} ⁵⁴:

$$k_{bl} = D_w / \delta \quad (7)$$

where D_w is the molecular diffusion coefficient of the compound in water with typical values ranging from 10^{-5} cm²/s to 10^{-6} cm²/s; and δ is thickness of the diffusive boundary layer, in most natural conditions $\delta \ll 1$ cm. δ in the microcosm test was measured to be 1.7 ± 0.2 mm by the alabaster method¹. The corresponding minimum of k_{bl} is 5.9×10^{-6} cm/s. Furthermore, the mass transfer coefficient reported by the field studies ranged from 2.8×10^{-5} cm/s to 4.6×10^{-4} cm/s^{61,62}. The mass transfer coefficients obtained in the laboratory experiments ranges from 1.5×10^{-6} cm/s to 5.1×10^{-5} cm/s,

187 which are much lower than those obtained by the field studies due to overestimation
 188 of pore water concentrations or artificially high fluxes^{63,64}. In this study, 2.5×10^{-5} ,
 189 5×10^{-5} and 10^{-4} cm/s will be used in the following analysis.

190 The initial conditions are assumed to be

$$191 \quad C_m(z,0) = C_{m,int}(z) \quad (m=1, 2, 3, \dots, M) \quad (8)$$

192 where $C_{m,int}$ is the initial concentration in soil layer m .

193 It should be pointed out that compared with the one-dimensional
 194 partial-differential equation considered in this study, much more complicated
 195 two-dimensional partial-differential equations have been considered in the process of
 196 deriving analytical solutions for both chemical and physical dissolution front
 197 instability problems in fluid-saturated porous media⁴³⁻⁴⁹. Therefore, the factors
 198 including solute dispersion, mineral dissolution ratio^{65,66}, medium permeability
 199 anisotropy⁶⁷, temperature effect^{68,69}, non-linear adsorption⁷⁰, complex degradation
 200 processes⁷¹, consolidation-induced advection⁷² were neglected in this study.

201 **Analytical solution**

202 The following dimensionless parameters are defined to derive the analytical solution
 203 of the proposed mathematical model:

$$204 \quad \omega = \frac{z}{l_i} \quad (9)$$

$$205 \quad C^* = \frac{C}{C_0} \quad (10)$$

$$206 \quad \tau = \frac{D_1^* t}{R_d l_1^2} \quad (11)$$

$$D_{am} = \frac{\lambda_m l_m^2}{D_m^*} \quad (m=1, 2, 3, \dots, M) \quad (12)$$

$$Sh = \frac{k_{bl} l_M}{D_M^*} \quad (13)$$

where ω , C^* and τ are dimensionless depth, dimensionless concentration and time factor, respectively. The Damköhler number (D_{am}) and Sherwood number (Sh) represent the ratio of reaction rate to the transport phenomena rate occurring in a system and the ratio of the total rate of mass transfer to the rate of diffusion, respectively⁵⁴.

The governing equation (1) can be rewritten in terms of the dimensionless parameters introduced above:

$$a_m \frac{\partial C_m^*}{\partial \tau} = \frac{\partial^2 C_m^*}{\partial \omega^2} - \frac{D_{am} C_m^*}{c_m^2} \quad (m=1, 2, 3, \dots, M) \quad (14)$$

where

$$a_m = \frac{R_{dm} D_1^*}{R_{d1} D_m^*} \quad (m=1, 2, 3, \dots, M) \quad (15)$$

$$c_m = \frac{l_m}{l_1} \quad (m=1, 2, 3, \dots, M) \quad (16)$$

The dimensionless boundary conditions are as follows:

$$C_m^* = C_{m+1}^* \quad (m=1, 2, 3, \dots, M-1) \quad (17)$$

$$n_m D_m^* \frac{\partial C_m^*}{\partial \omega} = n_{m+1} D_{m+1}^* \frac{\partial C_{m+1}^*}{\partial \omega} \quad (m=1, 2, 3, \dots, M-1) \quad (18)$$

$$\left. \frac{\partial C_M^*}{\partial \omega} \right|_{\omega=0} = 0 \quad (19)$$

$$\left. \frac{\partial C_1^*}{\partial \omega} \right|_{\omega=\frac{L_M}{l_1}} = Sh C_1^* \Big|_{\omega=\frac{L_M}{l_1}} \quad (20)$$

225 The initial condition is changed into

$$226 \quad C_m^*(z,0) = \frac{C_{m,\text{int}}(z)}{C_0} \quad (m=1, 2, 3, \dots, M) \quad (21)$$

227 Eq. (14) can be solved by the method of the classic integral transform technique

228 (CITT)⁷³. Following the systematized procedure of the CITT, an auxiliary

229 homogeneous problem for the space variable function $\psi_m(\omega)$ in the same

230 layers of the original problem needs to be defined. An auxiliary problem can be

231 obtained by applying separation of variables to Eqs. (14)-(21):

$$232 \quad -a_m \xi_i^2 \psi_m = \frac{\partial^2 \psi_m}{\partial \omega^2} - \frac{D_{am} \psi_m}{c_m^2} = H_m \psi_m \quad (m=1, 2, 3, \dots, M) \quad (22)$$

233 The operator H_m is defined as

$$234 \quad H_m = \frac{\partial^2}{\partial \omega^2} - \frac{D_{am}}{c_m^2} \quad (m=1, 2, 3, \dots, M) \quad (23)$$

235 And the boundary conditions are as follows:

$$236 \quad \frac{\partial \psi_1}{\partial \omega} = 0 \quad (24a)$$

$$237 \quad \psi_m = \psi_{m+1} \quad (m=1, 2, 3, \dots, M-1) \quad (24b)$$

$$238 \quad n_m D_m^* \frac{d\psi_m}{d\omega} = n_{m+1} D_{m+1}^* \frac{d\psi_{m+1}}{d\omega} \quad (m=1, 2, 3, \dots, M-1) \quad (24c)$$

$$239 \quad \frac{\partial \psi_M}{\partial \omega} = Sh \psi_M \quad (24d)$$

240 The above system is an eigenvalue problem and has nontrivial solutions for a discrete

241 spectrum of the eigenvalues $\xi_i (i=1, 2, 3, \dots, \infty)$. The general symbolic solution of Eq.

242 (22) can be written in terms of two linearly independent solutions $\phi_{m,i}(\omega)$ and $\theta_{m,i}(\omega)$:

$$243 \quad \psi_{m,i}(\omega) = A_{m,i} \phi_{m,i}(\omega) + B_{m,i} \theta_{m,i}(\omega) \quad (m=1, 2, 3, \dots, M) \quad (25)$$

244 where $A_{m,i}$ and $B_{m,i}$ are the parameters to be determined.

245 According to Eqs. (24a) and (25), the coefficients for the first layer can be obtained as
 246 follows:

$$247 \quad B_{1,i} = -\frac{\phi_{1,i}(0)}{\theta_{1,i}(0)} A_{1,i} \quad (m=1, 2, 3, \dots, M) \quad (26)$$

248 Substituting Eq.(25) into Eqs.(24) results in the following expressions for the
 249 coefficients $A_{m,i}$ and $B_{m,i}$:

$$250 \quad A_{m,i} = \left(\frac{A_{m-1,i}}{k_m} \right) \frac{k_m \phi_{m-1,i}(z_{m-1}^*) \theta'_{m,i}(z_{m-1}^*) - k_{m-1} \theta_{m,i}(z_{m-1}^*) \phi'_{m-1,i}(z_{m-1}^*)}{\phi_{m,i}(z_{m-1}^*) \theta'_{m,i}(z_{m-1}^*) - \theta_{m,i}(z_{m-1}^*) \phi'_{m,i}(z_{m-1}^*)} \\ + \left(\frac{B_{m-1,i}}{k_m} \right) \frac{k_m \theta_{m-1,i}(z_{m-1}^*) \theta'_{m,i}(z_{m-1}^*) - k_{m-1} \theta_{m,i}(z_{m-1}^*) \theta'_{m-1,i}(z_{m-1}^*)}{\phi_{m,i}(z_{m-1}^*) \theta'_{m,i}(z_{m-1}^*) - \theta_{m,i}(z_{m-1}^*) \phi'_{m,i}(z_{m-1}^*)} \\ 251 \quad (m=1, 2, 3, \dots, M) \quad (27)$$

$$252 \quad B_{m,i} = \left(\frac{A_{m-1,i}}{k_m} \right) \frac{k_{m-1} \phi_{m,i}(z_{m-1}^*) \phi'_{m-1,i}(z_{m-1}^*) - k_m \phi_{m-1,i}(z_{m-1}^*) \phi'_{m,i}(z_{m-1}^*)}{\phi_{m,i}(z_{m-1}^*) \theta'_{m,i}(z_{m-1}^*) - \theta_{m,i}(z_{m-1}^*) \phi'_{m,i}(z_{m-1}^*)} \\ + \left(\frac{B_{m-1,i}}{k_m} \right) \frac{k_{m-1} \phi_{m-1,i}(z_{m-1}^*) \theta'_{m-1,i}(z_{m-1}^*) - k_m \theta_{m-1,i}(z_{m-1}^*) \phi'_{m,i}(z_{m-1}^*)}{\phi_{m,i}(z_{m-1}^*) \theta'_{m,i}(z_{m-1}^*) - \theta_{m,i}(z_{m-1}^*) \phi'_{m,i}(z_{m-1}^*)} \\ 253 \quad (m=1, 2, 3, \dots, M) \quad (28)$$

254 where $k_m = n_m D_m^*$. The value of $A_{1,i}$ is arbitrary and is set to $A_{1,i} = 1$.

255 Eqs. (24d) and (25) are used to find a symbolic general transcendental equation.

$$256 \quad A_{M,i} \phi'_{M,i}(z_M^*) + B_{M,i} \theta'_{M,i}(z_M^*) = 0 \quad (29)$$

257 The general solution of the eigenvalue problem (Eq. 22) can be expressed as
 258 follows⁷³:

$$259 \quad \phi_{m,i}(\omega) = \sin(\beta_{m,i} \omega) \quad (m=1, 2, 3, \dots, M) \quad (30)$$

$$260 \quad \theta_{m,i}(\omega) = \cos(\beta_{m,i} \omega) \quad (m=1, 2, 3, \dots, M) \quad (31)$$

261 where $\beta_{m,i}$ are the layer eigenvalues, which are related to the eigenvalues ξ_i by

$$262 \quad \beta_{m,i} = \frac{(4\xi_i^2 a_m - 4D_{am} / c_m^2)^{1/2}}{2} \quad (m=1, 2, 3, \dots, M) \quad (32)$$

263 According to Eqs. (26) and (30)-(32), the coefficients for the first layer can be
 264 obtained as follows:

$$265 \quad B_{1,i} = 0 \quad (33)$$

266

267 For the others layers, the following recursive formulas are obtained:

$$268 \quad A_{m,i} = [A_{m-1,i} \cos(\beta_{m-1,i} z_{m-1}^*) - B_{m-1,i} \sin(\beta_{m-1,i} z_{m-1}^*)] \frac{k_{m-1} \beta_{m-1,i}}{k_m \beta_{m,i}} \\ + \sin(\beta_{m,i} z_{m-1}^*) [A_{m-1,i} \sin(\beta_{m-1,i} z_{m-1}^*) + B_{m-1,i} \cos(\beta_{m-1,i} z_{m-1}^*)] \\ 269 \quad (m=2, 3, \dots, M) \quad (34)$$

$$270 \quad B_{m,i} = \cos(\beta_{m,i} z_{m-1}^*) [A_{m-1,i} \sin(\beta_{m-1,i} z_{m-1}^*) + B_{m-1,i} \cos(\beta_{m-1,i} z_{m-1}^*)] \\ - \sin(\beta_{m,i} z_{m-1}^*) [A_{m-1,i} \cos(\beta_{m-1,i} z_{m-1}^*) - B_{m-1,i} \sin(\beta_{m-1,i} z_{m-1}^*)] \frac{k_{m-1} \beta_{m-1,i}}{k_m \beta_{m,i}} \\ 271 \quad (m=2, 3, \dots, M) \quad (35)$$

272 The eigenfunctions $\psi_{m,i}(\omega)$ can be expressed as follows:

$$273 \quad \psi_{m,i}(\omega) = A_{m,i} \sin(\beta_{m,i} \omega) + B_{m,i} \cos(\beta_{m,i} \omega) \quad (m=1, 2, 3, \dots, M) \quad (36)$$

274 Finally, using Eqs.(29)-(32) the following transcendental equation can be obtained:

$$275 \quad A_{M,i} \sin(\beta_{M,i} z_M^*) + B_{M,i} \cos(\beta_{M,i} z_M^*) = 0 \quad (37)$$

276 In the classification system given by Mikhailow and Ozisik⁷⁴ for self adjoint problems

277 of heat and mass diffusion, an eigenvalue problem is defined as:

$$278 \quad \frac{d}{dz} \left[\frac{d\psi_m}{dz} \right] + [\xi^2 w_m(\omega) - q_m(\omega)] \psi_m = 0 \quad (m=1, 2, 3, \dots, M) \quad (38)$$

279 where

$$280 \quad q_m(\omega) = \frac{D_m}{c_m^2} \quad (m=1, 2, 3, \dots, M) \quad (39)$$

$$281 \quad w_m(\omega) = a_m \quad (m=1, 2, 3, \dots, M) \quad (40)$$

282 The orthogonality property for the set of linearly independent eigenfunctions, $\psi_{m,i}(\omega)$,
 283 associated with Eq. (38) is given by:

$$284 \quad \sum_{m=1}^M \int_{z_{m-1}^*}^{z_m^*} w_m(\omega) \psi_{m,i}(\omega) \psi_{m,j}(\omega) d\omega = \delta_{ij} N_i \quad (m=1, 2, 3, \dots, M) \quad (41)$$

285 where N_i is the norm. The closed-form expression for the norm is as follows:

$$286 \quad N_i = \sum_{m=1}^M \bar{N}_{m,i} \quad (m=1, 2, 3, \dots, M) \quad (42)$$

287 where

$$288 \quad \bar{N}_{m,i} = \frac{a_m}{4\beta_{m,i}} \{ 2\beta_{m,i} (A_{m,i}^2 + B_{m,i}^2) (z_m^* - z_{m-1}^*) + 2A_{m,i} B_{m,i} [\cos(2\beta_{m,i} z_{m-1}^*) - \cos(2\beta_{m,i} z_m^*)] \\ + (A_{m,i}^2 - B_{m,i}^2) [\sin(2\beta_{m,i} z_{m-1}^*) - \sin(2\beta_{m,i} z_m^*)] \} \\ 289 \quad (m=1, 2, 3, \dots, M) \quad (43)$$

290 Representing the unknown function $C_m(\omega, \tau)$ as a series expansion in terms of the
 291 eigenfunctions $\psi_{m,i}(\omega)$ and using the orthogonality property (Eq. 42) results in the
 292 following integral transform pair:

$$293 \quad C_m(\omega, \tau) = \sum_{i=1}^{\infty} \frac{\psi_{m,i}(\omega)}{N_i} \bar{C}_i(\tau) \quad (m=1, 2, 3, \dots, M) \quad (44)$$

294 And its corresponding inverse transform is

$$295 \quad \bar{C}_i(\tau) = \sum_{m=1}^M \int_{z_{m-1}^*}^{z_m^*} w_m(\omega) \psi_{m,i}(\omega) C(\omega, \tau) d\omega \quad (m=1, 2, 3, \dots, M) \quad (45)$$

296 Applying the inverse formula (Eq. 34) to Eq. (14) and recalling the eigenvalue
 297 problem (Eq. 22) results in

$$298 \quad a_m \frac{\partial}{\partial \tau} \sum_{j=1}^{\infty} \frac{\psi_{m,i}(\omega)}{N_j} \bar{C}_j(\tau) = - \sum_{j=1}^{\infty} \frac{a_m \xi_j^2 \psi_{m,j}(\omega)}{N_j} \bar{C}_j(\tau) \quad (m=1, 2, 3, \dots, M) \quad (46)$$

299 Applying $\sum_{m=1}^M \int_{z_{m-1}^*}^{z_m^*} \psi_{m,i}(\omega) d\omega$ to both sides of Eq. (46) results in

$$\begin{aligned}
& \frac{\partial}{\partial \tau} \sum_{j=1}^{\infty} \frac{\bar{C}_j(\tau)}{N_j} \sum_{m=1}^M \int_{z_{m-1}^*}^{z_m^*} a_m \psi_{m,i}(\omega) \psi_{m,j}(\omega) d\omega \\
& = - \sum_{j=1}^{\infty} \frac{\bar{C}_j(\tau)}{N_j} \xi_j^2 \sum_{m=1}^M \int_{z_{m-1}^*}^{z_m^*} a_m \psi_{m,i}(\omega) \psi_{m,j}(\omega) d\omega
\end{aligned} \quad (m=1, 2, 3, \dots, M) \quad (47)$$

By using the orthogonality property (Eq. 42), the following equation can be obtained:

$$\frac{d\bar{C}_i(\tau)}{d\tau} = -\xi_i^2 \bar{C}_i(\tau) \quad (48)$$

The initial condition (Eq. 22) can also be transformed to yield

$$\bar{C}_i(0) = \sum_{m=1}^M \bar{f}_{m,i} \quad (m=1, 2, 3, \dots, M) \quad (49)$$

where

$$\bar{f}_{m,i} = \int_{z_{m-1}^*}^{z_m^*} w_m(\omega) \psi_{m,i}(\omega) C(\omega, 0) d\omega \quad (m=1, 2, 3, \dots, M) \quad (50)$$

Solving Eq.(48) with initial condition Eq.(49) gives the transformed field:

$$\bar{C}_i(\tau) = \bar{C}_i(0) \exp(-\xi_i^2 \tau) \quad (51)$$

Finally, invoking the inverse formula Eq.(42) and the relationship in Eq.(51) the closed-form analytical solution is obtained as follows:

$$C_m(\omega, \tau) = \sum_{i=1}^{\infty} \frac{\psi_{m,i}(\omega)}{N_i} \bar{C}_i(0) \exp(-\xi_i^2 \tau) \quad (m=1, 2, 3, \dots, M) \quad (52)$$

The flux of at the surface of the cap can be obtained as

$$J(L_M, \tau) = -n_M D_M^* \frac{\partial C_1(L_M, \tau)}{\partial \omega} \quad (53)$$

Substituting Eq. (52) into Eq. (53) results in

$$J(L_M, \tau) = -n_M D_M^* \sum_{i=1}^{\infty} \frac{A_{1,i} \cos(\beta_{1,i} \omega) + B_{1,i} \sin(\beta_{1,i} \omega)}{N_i} \bar{C}_i(0) \exp(-\xi_i^2 \tau) \beta_{1,i} \quad (54)$$

The cap effectiveness factor, which can be used as the assessment of the cap performance, can be expressed as follows:

$$CE = \frac{J_{uc} - J_c}{J_{uc} + J_c} \quad (55)$$

where J_{uc} and J_c are the (hypothetical) uncapped fluxes and capped fluxes at the top of the cap system, respectively.

4. Results and discussions

4.1. Good experimental set-up to verify the model.

Fig. 2a and 2b presents the comparison of the results of the proposed analytical models with experimental data obtained from laboratory-scale simulations of capped contaminated sediment⁴. In the experiments, the contaminated sediment layer in the two cases was obtained from the lake bottom located at the Louisiana State University campus in Baton Rouge. In the two cases, the cap materials are Balsam sand cap and Tao River sand cap, respectively. The balsam sand is a proposed cap material from a quarry near New Bedford and The Tao River sample was obtained from the bed of the Yellow River in China. The retardation factors for the Balsam sand and Tao River sand cap are 4.94 and 8.3, respectively. The effective diffusion coefficients of the Balsam sand and Tao River cap are 7×10^{-10} and 8.3×10^{-10} m²/s, respectively⁶. In the experiments, 1.5-cm-thick sediment was contaminated by trichloropropane (TCP) and covered by a 0.7-cm-thick capping layer to impede the TCP from diffusing into the surface water. The transport properties for these two layers are summarized in Table 1. The initial concentration of TCP in the sediment and the capping layer is 150 mg/L and 0, respectively. A zero-flux boundary condition is imposed at the bottom of the sediment layer. The concentration remains zero at the top of the capping layer to

model the flushing effect of the surface water. The half-life of TCP is 30-60 years reported by Thoma et al.⁶. The half-life of TCP in capping and sediment are assumed to be 100 years in this case. The solid line is the predicted flux by the proposed analytical model and the dot is the experimental data from laboratory-scale simulations (see Fig.2). It can be seen that the predicted flux is in good agreement with the experimental data for both of the capped systems. This indicates that the proposed analytical solutions are rational and can yield correct results.

4.2 Dimensionless analysis of contaminant diffusion in capped contaminated sediments

The soil and transport properties considered for these four layers are summarized in Table 2. A zero-flux boundary condition is assumed at the bottom of the sediment layer, and the Robin-type boundary condition and zero concentration boundary condition are assumed at the top of the capping layer.

Fig. 3 shows the dimensionless concentration profiles for different Damköhler numbers at time factor $\tau = \frac{D_1^* t}{R_{d1} l_1^2} = 0.01$. $D_{a4} = \frac{\lambda_4 l_4^2}{D_4^*}$ is Damkohler number in the bioturbation layer. The experimental data from Gilevska et al.⁷⁵ showed that biodegradation rate of contaminant in bioturbation layer ranges from 0.4 year⁻¹ to 84 year⁻¹. Damkohler number in the bioturbation layer (D_{a4}) here is assumed to be 1, 5, 10 and 30, respectively. The relative concentration in the capping layer is significantly reduced with the increase of D_{a4} . For example, the relative concentration at the surface of sand layer for the case with $D_{a4}=1$ can be 2.8 times greater than that of the case with $D_{a4}=30$. The above analysis indicated that considering the effect of

contaminant biodegradation in bioturbation layer can improve the efficiency of the capping systems.

Fig. 4 shows the effect of $a_2 = \frac{R_{d2}D_1^*}{R_{d1}D_2^*}$ and $Da_4 = \frac{\lambda_4 l_4^2}{D_4^*}$ on cap effectiveness factor. Five cases including case 1 ($a_2=2.26, Da_4=1$), case 2 ($a_2=2.26, Da_4=5$), case 3 ($a_2=2.26, Da_4=10$), case 4 ($a_2=11.3, Da_4=1$) and case 5 ($a_2=22.6, Da_4=1$) were selected to analyze the effects of different combinations a_2 and Da_4 on cap effectiveness factor. The parameter a_2 has a less significant effect on the cap effectiveness factor than that of Da_4 . For instance, the time required for CE to reach 0.5 for case 1 can be 1.8 and 50 times less than that of case 2 and case 5, respectively. This is due to the fact that the sorbent layer is relatively thin and the diffusion barrier effect is also weak. It can be seen that the cap effectiveness factor significantly increases with the increment of Da_4 . For example, the time factor required for CE to reach 0.5 for case 1, case 2 and case 3 is 0.02, 1.05 and 2.12, respectively. When $\tau=1$, the effectiveness factor for the case 2 and case 3 is 0.5 and 0.8, respectively. It indicates that biodegradation of contaminant in bioturbation layer can effectively decrease flux released from capped contaminated sediment.

Fig.5a and 5b show the effect of sorbent layer on relative concentration over time at surface of sand layer for different a_2 and c_2 . The effective remediation time was designed to be the time for the concentration at the top of the sand layer to reach 10% of initial contaminant concentration². It can be seen that both of the dimensionless retardation factor a_2 and dimensionless thickness c_2 have a great influence on contaminant transport in the capping system. The effective remediation

time for the case with $a_2=100$ can be 22.7 times larger than that with $a_2=10$ (Fig.5a). The time required to reach the maximum relative concentration for the case with $a_2=20$ can be 11.2 times larger than the case with $a_2=1$. Furthermore, the maximum relative concentration for the case with $a_2=20$ can be around 1.9 times less than the case with $a_2=1$. As for c_2 , the effective remediation time and the time required to reach the maximum relative concentration for the case with $c_2=0.01$ can be around 10 times larger than $c_2=0.05$, respectively (Fig.5b). If the capping system is designed to be effective for a 200-year period which equals to $\tau=0.02$, the reasonable value of a_2 should be larger than 50 under $c_2=0.03$ for the in-situ capping system (Fig.5a). Similarly, the reasonable value of c_2 should be larger than 0.05 under $a_2=20$ (Fig.5b). The above analysis indicates that the proposed dimensionless analytical model can be used to design a final capping system. The results also indicate that capping will be an attractive alternative for remediation when the adsorption factor and the thickness of sorbent layer are well designed⁷.

4.3 Effect of sorbent layer and bioturbation layer on flux at surface of system

Fig. 6 shows the effect of sorbent layer on the flux at surface of the system ($z=L_M$). Five cases including case 1 (without sorbent layer), case 2 ($l_{sorbent}=5\text{mm}$, and $R_{d2}=260$), case 3 ($l_{sorbent}=10\text{mm}$ and $R_{d2}=130$), case 4 ($l_{sorbent}=10\text{mm}$, $R_{d2}=260$) and case 5 ($l_{sorbent}=20\text{mm}$, $R_{d2}=130$) are selected to analyze the effects of retardation factor and thickness of sorbent layer on surface flux. For each case, there is a period of time before any contaminant has transported through the cap system (isolation time), followed by a period of increasing flux through the cap and into the bioactive zone

until a maximum is reached, and then a decrease in flux over time until the underlying sediment layer is depleted⁵. The isolation time is defined as the time when the flux of contaminant at the top of the cap system reaches 10% of the maximum flux simulated in that case. The isolation time for case 1, case 2, case 3, case 4 and case 5 is 3.1 years, 5.2 years, 6.4 years, 9 years and 17 years, respectively. The maximum flux for case 1 can be 1.8 times larger than that of case 4. However, the time required to reach the maximum flux for case 1 can be 7.5 times less than that of the case 4. The above results show that increasing the adsorption properties and thickness of sorbent layer would result in an effective improvement of the cap system. The isolation time for case 5 can be 2.7 and 1.9 times longer than that of case 3 and case 4, respectively. Furthermore, the maximum flux for case 2 can also be 1.1 times larger than that of case 3. The above analysis indicates that increasing the thickness of sorbent layer might be more effective than that of the improvement of adsorption factor in sorbent layer.

Fig. 7a and 7b show the effect of bioturbation layer on the flux at the surface of system under different half-lives of contaminant and thicknesses of bioturbation layer. Bioturbation is the normal life cycle activity of benthic organisms that lead to mixing of sediment and porewater in the near surface layer of sediments. These activities have a great influence on the fate and behavior of contaminants. They are often the dominant mixing process in stable sediment environments⁷⁶. Thoms et al.⁷⁷ summarizes the literature reported values of the depth of bioturbation at more than 200 sites via a variety of different organisms. It is indicated that the bioturbation depth

427 for freshwater and estuarine systems are approximately 3.1cm and 14.8cm,
 428 respectively. The biodiffusion coefficients are around $1 \times 10^{-5} \text{ cm}^2/\text{s}$ and $5 \times 10^{-4} \text{ cm}^2/\text{s}$
 429 for freshwater and estuarine systems, respectively⁷. In order to assure that the
 430 designed cap can meet the requirement of the quantitative goals, it is important to
 431 analyze how the height of bioturbation layer and biodegradation of contaminant can
 432 affect the performance of a cap. The range of biodegradation rate in bioturbation layer
 433 is assumed to be from 0.4 year^{-1} to 84 year^{-1} . The corresponding half-life in the
 434 bioturbation layer $t_{1/2,bio}$ ranges from 0.008 to 1.73 years⁷⁵. The flux at surface of
 435 system is significantly reduced with a decrease of half-life of contaminant. For
 436 example, the maximum flux for the case with $t_{1/2,bio} = 0.07 \text{ year}$ can be 4.5 times less
 437 than that of the case without considering the effect of biodegradation (Fig.7a).
 438 However, the biodegradation of contaminant shows a less important influence on the
 439 isolation time. For instance, the isolation time for the case with $t_{1/2,bio} = 0.07 \text{ year}$ and
 440 case with $t_{1/2,bio} = 0.7 \text{ year}$ is 12.7 years and 11.2 years, respectively. The thickness of
 441 bioturbation layer also has a great influence on flux at surface of system. For example,
 442 the maximum flux for the case with $l_{bio} = 15 \text{ cm}$ can be 1.5 times greater than that of the
 443 case with $l_{bio} = 5 \text{ cm}$. Increasing the thickness of bioturbation layer would result in a
 444 decrease of the maximum contaminant flux dispersing into water. This is due to the
 445 fact that the effective contaminant transport pathway increases with the increment of
 446 bioturbation layer. In addition, degradation of contaminant can play a more significant
 447 role when bioturbation layer has a larger thickness. However, the maximum flux for
 448 the case with $l_{bio} = 15 \text{ cm}$ can be 17 times larger than that of the case without

bioturbation layer. This may be due to the fact that the effective diffusion coefficient of sand cap is 28 times lower than D_{bio} . The result from the model was in accordance with the experimental studies⁷⁸. Granberg et.al.⁷⁹ also showed that bioturbation can stimulate an augmented release flux of PCBs.

Fig.8a and Fig.8b show the flux at the surface of system under different combinations of properties of sorbent layer and bioturbation layer. The case with $t_{1/2,bio}=0.7$ year and $R_{dsorbent}=260$ is selected as a reference case to investigate the relative importance of biodegradation rate in bioturbation layer and retardation factor in sorbent layer (Fig.8a). It can be seen that the maximum flux for the reference case can be 3.6 and 1.9 times larger than the cases with $t_{1/2,bio}=0.07$ year, $R_{dsorbent}=260$ and $t_{1/2,bio}=0.7$ year, $R_{dsorbent}=2600$, respectively. The isolation time for the case with $t_{1/2,bio}=0.7$ year and $R_{dsorbent}=2600$ can be 4.3 times larger than the case with $t_{1/2,bio}=0.7$ year and $R_{dsorbent}=260$. The above results indicate that increasing half-life of contaminant in bioturbation layer can significantly reduce the contaminant flux at the surface of system. However, the increase of half-life of contaminant in bioturbation layer has a negligible effect on isolation time. On the contrary, increasing retardation factor in sorbent layer can effectively extend the isolation time although retardation factor has a less influence on surface flux. The case with $l_{bio}=10\text{cm}$ and $l_{sorbent}=1\text{mm}$ is selected as a reference case to investigate the relatively importance of thickness of bioturbation layer and sorbent layer (Fig.8b). The maximum flux for the reference case can be 1.7 and 1.3 times larger than the case with $l_{bio}=20\text{cm}$, $l_{sorbent}=1\text{mm}$ and $l_{bio}=10\text{cm}$, $l_{sorbent}=2\text{mm}$, respectively. The isolation time for the case with $l_{bio}=10\text{cm}$, $l_{sorbent}=2\text{mm}$

is 25 years. The isolation time for the reference case and the case with $l_{bio}=20\text{cm}$, $l_{sorbent}=1\text{mm}$ are 13 years and 15 years, respectively. The above results indicate that surface flux is sensitive to biodegradation rate and thickness of bioturbation layer although the properties of bioturbation layer have a weak effect on the isolation time. However, the properties of sorbent layer include retardation factor and thickness have a significant influence on both surface flux and isolation time. The above analysis also indicates that increasing the adsorption properties and thickness of sorbent layer would result in an effective improvement of the cap system.

4.4 Effect of mass transfer coefficient

Fig. 9a and 9b show the effect of the mass transfer coefficient on contaminant concentration and flux at the surface of system. The mass transfer coefficient is in inverse proportion to the thickness of the effective diffusive boundary layer (DBL). This DBL is the thin layer of water adjacent to the sediment surface through which molecular diffusion is the dominant transport mechanism for dissolved material⁸⁰. $k_{bl}=2.5\times 10^{-5}\text{ cm/s}$, $5\times 10^{-5}\text{ cm/s}$ and 10^{-4} cm/s are used in the following analysis (according to Eq.7). The effect of mass transfer coefficient on the contaminant concentration over time at the surface of system was shown in Fig. 9a. At the top of the bioturbation layer, the maximum contaminant concentration for the case with $k_{bl}=2.5\times 10^{-5}\text{ cm/s}$ can reach 0.26 mg/L, which is 13 times larger than that of the case with $k_{bl}=10^{-4}\text{ cm/s}$. The surface contaminant concentration decreases with the increase of the mass transfer coefficient since the thickness of the DBL also decreases with the increase of the mass transfer coefficient. It indicates that considering the effect of k_{bl}

(<10⁻⁴ cm/s) may reduce the performance of the cap. Fig. 9b shows the effect of the mass transfer coefficient on contaminant flux over time at the surface of the bioturbation layer. The contaminant flux at the top of bioturbation layer increases with the increase of k_{bl} . For example, the maximum contaminant flux for the case with $k_{bl}=10^{-4}$ cm/s can be 1.3 and 1.1 times greater than that of the case with $k_{bl}=2.5\times10^{-5}$ cm/s and 5×10^{-5} cm/s, respectively. The result from the model agrees with the experimental studies which showed that larger mass transfer coefficient results in a greater flux⁸¹. This is due to the fact that the increment in the concentration gradient induced by the increase of mass transfer coefficient augments the contaminant flux at the surface of system.

5. Summary and conclusions

An analytical model for contaminant transport in multi-layered capped contaminated sediment considering the degradation of organic contaminant was presented. The results obtained by the proposed analytical model agree well with those obtained from the laboratory tests. Based on the analytical model, the effects of half-life of contaminant in bioturbation, thickness of bioturbation layer, retardation factor of sorbent layer, thickness of sorbent layer and mass transfer coefficient on contaminant transport in capped contaminated sediment system were analyzed. The conclusions are as follows:

- (1) The properties of bioturbation layer have a significant effect on the performance of the capped contaminated sediment system. The maximum flux for the case with $t_{1/2,bio}=0.07$ year can be 4.5 times less than that of the case without considering the

effect of biodegradation. The effectiveness factor for the case with $D_{a4}=10$ can be 1.6 times than that with $D_{a4}=5$. This indicated that the effect of contaminant biodegradation in bioturbation layer should be considered for the design of the capping system.

(2) Increasing the thickness of sorbent layer might be more effective on improving isolation time than that of the increment of adsorption factor in sorbent layer. The isolation time for the case with $l_{sorbent}=10\text{mm}$, $R_{dsorbent}=130$ can be 1.4 and 2.7 times less than that of case $l_{sorbent}=10\text{mm}$ and $R_{dsorbent}=260$ and $l_{sorbent}=20\text{mm}$, $R_{d2}=130$, respectively. Increasing the biodegradation rates of contaminant in bioturbation layer is more effective on the decrease of surface flux than that of the increment of adsorption factor in sorbent layer. The surface maximum flux for the case with $t_{1/2,bio}=0.7$ year, $R_{dsorbent}=260$ can be 3.4 and 1.9 times larger than the cases with $t_{1/2,bio}=0.07$ year, $R_{dsorbent}=260$ and $t_{1/2,bio}=0.7$ year, $R_{dsorbent}=2600$, respectively.

(3) The mass transfer coefficient should be considered for the design of the capping system. At the top of the bioturbation layer, the maximum contaminant concentration at the surface of system for the case with $k_{bl}=2.5\times 10^{-5}$ cm/s can be 13 times larger than that of the case with $k_{bl}=10^{-4}$ cm/s.

(4) It should be noted that this study has certain limitations. For example, some important factors, such as solute dispersion⁶¹, mineral dissolution ratio⁶², medium permeability anisotropy⁶³, temperature effect^{64,65}, non-linear adsorption⁶⁶, complex degradation processes⁶⁷, advection and consolidation-induced

537 advection⁶⁸ were neglected in this study. To further improve the analytical
538 solutions derived from this study, these factors need to be considered in the future
539 study.

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546 **Notations**

547	$C_m(z, t)$	Concentration of contaminant
548	D_m^*	Effective diffusion coefficient
549	D_{am}	Damköhler number
550	$F_m(x)$	Concentration distribution of the contaminant in soils
551	$J_m(z, t)$	Mass flux
552	k_{bl}	Mass transfer coefficient in the benthic boundary layer
553	l_m	Thickness of the soil layer m
554	R_{dm}	Retardation factor
555	Sh	Sherwood number
556	t	Time
557	$t_{1/2}$	Half-life of contaminant in soil
558	$U_c(t)$	Average degree of diffusion

559	z	Space coordinate
560	λ_i	Biodegradation rate
561	ω	Dimensionless depth
562	τ	Time factor
563	ψ_m	Eigenfunction
564	ξ_i	Eigenvalues
565	β_m	The layer eigenvalues
566		

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806

Tab.1. Transport properties for capping layer and contaminated sediment for comparison with experimental data

	Balsam sand cap	Tao river cap
Cap properties		
D_w (m ² /s)	7×10^{-10}	8.3×10^{-10}
n_1	0.38	0.5
R_{d1}	4.95	8.7
L_1 (m)	0.7	0.7
$t_{1/2,capping}$ (year)	100	100
Sediment properties		
n_2	0.45	0.45
R_{d2}	50.5	55
L_2 (m)	1.5	1.5
$t_{1/2,sediment}$ (year)	100	100
Initial TCP concentration	150	150
(mg/L)		

811

812 **Tab. 2.** Parameters used in a layered sediment cap system simulations

Parameters	$L_f(\text{m})$	$D^*(\text{m}^2/\text{s})$	R_d	$t_{1/2}(\text{year})$
Bioturbation layer	0.1 ^a	2.8×10^{-9} ^c	10 ^c	1 ^d
Cap layer	0.05 ^a	1.0×10^{-10} ^b	8.7 ^c	70
Sorbent layer	0.01 ^a	1.0×10^{-10} ^b	260 ^c	70
Contaminated sediment	0.5 ^a	1.02×10^{-10} ^b	115 ^c	70 ^b

813 a: Murphy et al.⁵; b: Bortone et al.¹⁵; c: Go et al.⁷; d: Gilevska et al.⁷¹

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